Impact of Stepwise Desulfation on the Performance of a Ba-Based Commercial Lean NOx Trap Catalyst

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Introduction
The Lean NOx Trap (LNT) is being implemented in lean-burn vehicles for NOx aftertreatment. However, for its broader deployment, significant technical improvement is necessary especially with respect to sulfur poisoning. The LNT NOx storage components (Ba, K) have greater affinity for exhaust sulfur, and thus progressively lose their NOx storage capacity over time. As a result, high-temperature reductant-rich exhaust conditions are created periodically to “desulfate” the catalyst and regain its performance. The challenge is to develop more S-resistant LNTs and more effective strategies to desulfate while minimizing the fuel penalty and thermal aging arising from these high temperature excursions. Meeting this challenge will require deeper insights into how sulfation/desulfation affects LNT catalysis under relevant conditions. In addition to NOx storage materials, practical LNTs contain various other functions such as precious metals (Pt, Pd, Rh), (Al2O3, CeO2, TiO2), and oxygen storage capacity (CeO2-ZrO2). These components, through complex spatiotemporal interplay, determine LNT performance. Previously, we found that several LNT functions can be affected by S and proposed a conceptual model correlating spatiotemporal reaction distribution and global performance of a commercial LNT [1]. In this work, we addressed the desulfation aspect of the same LNT to further clarify the nature, distribution and roles of different S species by assessing the influence of stepwise desulfation on LNT performance.

Materials and Methods
A commercial Umicore LNT was evaluated on a bench reactor; details of the catalyst and reactor can be found in [1]. From ICP, XRD, EPMA, and TEM analyses, the catalyst was found to contain mainly two distinct domains: i) “active LNT” comprising Pt, Pd, Rh, Ba supported on CeO2-ZrO2; and ii) MgAl2O4. A fresh sample was degreased via hydrothermal treatment and six sulfation/desulfation steps to obtain reproducible performance. Total NOx storage capacity (lean portion of 15/10-min lean/rich long cycling), NOx conversion and NH3/N2O selectivity (both from 60/5-s lean/rich short cycling) were determined at 400˚C before and after sulfation (3.4 g/L) and after each of four consecutive desulfation steps (temperature ramp at 5˚C/min from 400˚C to maximum temperature Tmax = 492, 525, 564, 690˚C). The lean phase contained 300 ppm NO, 10% O2, 5% H2O, 5% CO2 and N2 balance, while the rich phase contained H2 (0.4% for long and 3.4% for short cycling), 5% H2O, 5% CO2 and N2 balance. The gas composition was determined by FT-IR, SO2/H2S analyzers, and SpaciMS. The sample was characterized using various techniques including DRIFTS.

Results and Discussion
Sulfation decreased NOx storage and conversion, but increased NH3 selectivity (Fig.1). This increased NH3 was previously explained by reduced oxidation of NH3 by downstream oxygen storage components based on spatially resolved gas analyses using SpaciMS [1]. Briefly, the plug-like poisoning of Ba sites resulted in an axial displacement of the NH3-forming NOx–storage-reduction zone and concomitant shortening of the downstream oxygen-storage-only zone. The consecutive desulfation steps progressively reversed these trends (Fig. 1). However, the relationship between incremental S removal and resultant performance recovery was not linear. For example, the first desulfation step (Tmax = 492˚C) produced insignificant performance recovery despite 46% S removal. The S removed in this first step was primarily associated with CeO2-ZrO2 and other supports in the catalyst front. The implication is that this “containment” of 46% S in the catalyst front minimized S impact on downstream NOx storage sites. The slight degradation of short cycling performance (Figs. 1b and 1c) is likely due to partial readesorption of the upstream-released S onto downstream NOx storage sites. The 2nd and 3rd steps together removed only 26% S, but resulted in major recovery of NOx conversion and NH3/N2O selectivity. A remarkable impact of the 4th step (Tmax = 690˚C; removal of remaining 28% S) is the recovery of over 50% of the total NOx storage capacity with minor impact on NOx conversion and NH3/N2O selectivity.

![Figure 1](image-url)

**Figure 1.** Performance of a Ba-based commercial LNT as a function of desulfation extent: (a) total sulfur removal and recovery of total NOx storage capacity, (b) cycle-averaged NOx conversion, and (c) cycle-averaged NH3 and N2O selectivities.

Based on characterization (TPR, SpaciMS etc.), we attributed S from the 2nd through 4th steps to Ba sulfates. It follows that only a small portion of Ba was necessary to achieve full conversion under short cycling conditions. NOx selectivity remained low throughout the experiments. Interestingly, NOx and NH3 followed opposite trends suggesting that NOx might be a minor product of oxidizing upstream-formed NH3 by downstream oxygen species. In this presentation, we will discuss in detail the nature and distribution of different sulfur species and how their mobility under desulfation conditions affects local and global LNT performance.

Significance
This work provides fundamental insights on how desulfation at different temperatures affects the distribution of sulfur species and as a result the global performance of a commercial LNT. The findings will be useful to design, model and implement real LNTs.

Reference